

**Modeling of  
boundary layer  
interaction between  
NO<sub>2</sub> and bromine**

E. Tas et al.

# Measurement-based modeling of bromine chemistry at the Dead Sea boundary layer – Part 2: The influence of NO<sub>2</sub> on bromine chemistry at mid-latitude areas

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## Abstract

Understanding the interaction between anthropogenic air pollution and Reactive Halogen Species (RHS) activity has had only limited support of direct field measurements, due to the fact that past field measurements of RHS have been mainly performed in Polar Regions. The present paper investigates the interaction between  $\text{NO}_2$  and Reactive Bromine Species (RBS) activity by model simulations based on extensive field measurements performed in the Dead Sea area, as described in a companion paper (Tas et al., 2006). The Dead Sea is an excellent natural laboratory for this investigation since elevated concentrations of  $\text{BrO}$  (up to more than 150 pptv) are frequently observed, while the average levels of  $\text{NO}_2$  are around several ppb. The results of the present study show that under the chemical mechanisms that occur at the Dead Sea, higher levels of  $\text{NO}_2$  lead to higher daily average concentrations of  $\text{BrO}_x$ , as a result of an increase in the rate of the heterogeneous decomposition of  $\text{BrONO}_2$  that in turn causes an increase in the rate of the “Bromine Explosion” mechanism. The present study has shown that the influence of  $\text{NO}_2$  on  $\text{BrO}_x$  production clearly reflects an enhancement of RBS activity caused by anthropogenic activity. However, above a certain threshold level of  $\text{NO}_2$  (daily average mixing ratios of 0.2 ppbv during RBS activity), the daily average concentrations of  $\text{BrO}_x$  decrease for a further increase in the  $\text{NO}_2$  concentrations.

## 1 Introduction

The destruction of ozone in the tropospheric boundary layer of Polar Regions by Reactive Halogen Species (RHS) has been well documented during the last two decades (Barrie et al., 1988; Wessel et al., 1998; Murayama et al., 1992; Hausmann and Platt, 1994; Tuckerman et al., 1997; Kreher et al., 1997). It has been shown that Reactive Bromine Species (RBS) activity, with  $\text{BrO}$  levels up to  $\sim 30$  ppt play a major factor in boundary layer ozone depletion events (ODE's) (Platt and Hoenninger, 2003). Recently

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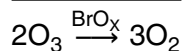
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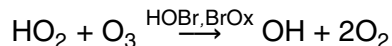
it has been recognized that RBS may also lead to ozone destruction in the boundary layer also at mid-latitude areas. This was evident for the first time at the Dead Sea where very high BrO levels, above 150 ppt, were detected together with daytime depletion of O<sub>3</sub> from levels of above 120 ppb to below the detection limit of the instrument (<1 ppb) (Hebestreit et al., 1999; Matveev et al., 2001). Later, evidence for additional RBS activity has been found at other mid-latitude locations. At the Great Salt Lake, Utah (Stutz et al., 2002), north of the Canary Islands (Leser et al., 2003) and at Salar de Uyuni, Bolivia (Hoenninger et al., 2004).

A companion paper (Tas et al., 2006), presented a chemical mechanism that could account for the RBS activity observed at the Dead Sea. The efficient destruction of ozone through the gas phase was described by the following two well known cycles:

#### Cycle 1 (BrO-cycle)



#### Cycle 2 (HOBr-cycle)



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In these chemical cycles, ozone is catalytically destroyed by Br and BrO ( $\text{BrO}_x$ ), while at the Dead Sea, Cycle 1 is more efficient due to the high BrO levels prevalent in this area (Tas et al., 2006). The above is the chemical basis that enables the destruction of ozone within a time scale of a few hours, by RHS, at concentrations three orders of magnitude smaller than ozone. However, it has been suggested (e.g., Lehrer et al., 2004) that the above mechanisms could not explain the observed  $\text{O}_3$  destruction rate in the troposphere, if the loss reactions of  $\text{BrO}_x$  with hydrocarbons were also taken into account.

In order to account for the observed  $\text{BrO}_x$  production and ozone destruction rates at the Dead Sea, more efficient recycling of bromine reservoirs via heterogeneous processes had to be included in the chemical mechanism. This is consistent with other studies (Tang and McConnell, 1996; Sander et al., 1997; De Haan et al., 1999; Michalowski et al., 2000; Pszenny et al., 2004).

It has been shown that the inclusion of the heterogeneous decomposition of  $\text{BrONO}_2$  on sulfate aerosols into the mechanism (Hanson and Ravishankara, 1995; Hanson et al., 1996; Sander et al., 1999) can significantly increase  $\text{BrO}_x$  formation through the production of HOBr. The inclusion of this heterogeneous process together with the “Bromine Explosion” mechanism (Mozurkewich et al., 1995; Vogt et al., 1996; Tang and McConnell, 1996; Platt and Moortgat., 1999) can account for the observed RBS activity at the Dead Sea. These two processes can be described by the following Cycle 3b (Tas et al., 2006):

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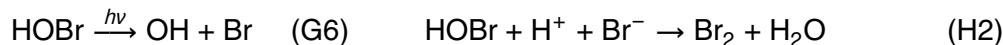
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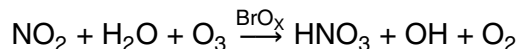
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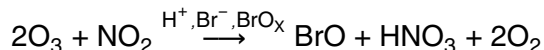
## Cycle 3



net: Cycle 3a



Cycle 3b



Cycle 3b is important because it leads to a nearly exponential growth of Br production via reaction H2, which represents the “Bromine Explosion” mechanism. The importance of the heterogeneous decomposition of  $\text{BrONO}_2$ , under the Dead Sea conditions, is that it leads to the enhancement of reaction H2 (the rate limiting step in Cycle 3b) by producing HOBr approximately 4 times faster in comparison with reaction (G5).

Based on kinetic considerations the rate of Cycle 3b is enhanced by the concentrations of  $\text{NO}_2$  and sulfate aerosols (Tas et al., 2006). This influence of  $\text{NO}_2$  and sulfate

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aerosols on the rate of Cycle 3b is of special importance since it represents the influence of anthropogenic activity on the rate of  $\text{BrO}_x$  production. In practice, the influence of  $\text{NO}_2$  levels on the rate of Cycle 3b is more significant since in general, its concentrations change more sharply with the distance from emission sources, than these of  $\text{SO}_2$ .

The present research investigates the influence of  $\text{NO}_2$  on the diurnal profile and total daily production of  $\text{BrO}_x$  and ozone destruction, caused primarily by the heterogeneous decomposition of  $\text{BrONO}_2$ . The sensitivity of  $\text{BrO}_x$  production to  $\text{NO}_2$  levels via the heterogeneous decomposition of  $\text{BrONO}_2$  has been investigated by Sander, et al. (1999), who showed that the increase in  $\text{NO}_2$  did not necessarily lead to an increase in the production of  $\text{BrO}_x$  via the heterogeneous decomposition of  $\text{BrONO}_2$ . In the present research this issue is investigated based on simulations performed by Tas et al. (2006) in order to explain the RBS activity at the Dead Sea area.

The effects of anthropogenic activity on RBS activity has had only limited support from direct field measurements, due mainly to the fact that past field measurements of RBS have been performed only in Polar Regions. The Dead Sea basin therefore provides a unique natural laboratory for investigating the interaction between RBS and photochemical pollutants, since very intensive RBS activity ( $\text{BrO}$  levels up to more than 150 pptv) is frequently observed in this area (Tas et al., 2003; Tas et al., 2005). In general, photochemical air pollution in this area can be characterized by average levels of  $\text{NO}_2$  and  $\text{SO}_2$  around several ppb. The research summarized in this paper contributes to the overall understanding of the influence of anthropogenic activity on RBS activity and ozone destruction at mid-latitude areas.

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## 2 Experimental

### 2.1 Model simulations

All of the simulations presented in Sects. 3.1 and 3.2 are based on the methods and parameters that were used in the “FULL” and the “NOB” simulations described previously in Tas et al. (2006). These simulations will be briefly described in the following. The “FULL” simulation is based on the parameters that were measured at the Dead Sea (Sect. 2.2) and lead to a relatively good agreement with measurements. The difference between the two simulations is that the “FULL” simulation includes the bromine chemistry while in the “NOB” simulation the bromine mechanism is absent. The two simulations were performed by a one dimensional chemical transport model (UAHCTM\_1D) (Biazar, 1995), which includes an explicit chemical gas phase mechanism and takes into account the vertical motion of the different species based on diffusion and advection calculations as well as on deposition velocity values. In the model the basic photochemical processes are described by 166 gas-phase reactions based on the Trainer mechanism (Trainer et al., 1987), and updated according to Atkinson et al. (2003). Thirty-one reactions, including five photochemical reactions were added to describe the bromine gas phase mechanism. Two heterogeneous processes, the heterogeneous decomposition of  $\text{BrONO}_2$  (H1) and the “Bromine Explosion” mechanism (H2) were also added. For the “FULL” simulation the assumptions were that reaction H1 occurred only on sulfate aerosols while reaction H2 occurred only inside sea salt aerosols.

All of the results and discussion presented in Sect. 3.1 are directly based on the “FULL” simulation, while the results and discussion presented in Sect. 3.2 are based on a set of simulations based on the “FULL” simulation and on the “NOB” simulation, while changing only the  $\text{NO}_2$  fluxes as described in more detail in Sect. 3.2. Note that in the paper, the magnitude  $\frac{\Delta X}{\Delta t}$  represents the rate of reaction number  $X$ , according to explanations given in Tas et al. (2006). This magnitude stands for the first derivative with time ( $t$ ) of an inert species ( $X$ ) that was added to the actual products of each

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reaction in the model. As described previously (Tas et al., 2006), it provides a direct measure of the contribution of each reaction to the formation of its products.

## 2.2 Field measurements

5 The 'FULL' and 'NOB' simulations were based on a comprehensive set of atmospheric trace gas measurements and relevant meteorological parameters collected at the Dead Sea as described in Tas et al. (2006). The methods used for these simulations will be briefly described in the following. Continuous measurements of  $O_3$ ,  $NO$ ,  $NO_x$ ,  $SO_2$ , particulate sulfates and nitrates, wind speed and direction, temperature, relative humidity, pressure and solar radiation, were conducted at the evaporation ponds using  
10 the techniques described by Matveev et al. (2001) during 2–12 August 2001. The differential optical absorption spectroscopy (DOAS) technique was employed to quantify  $BrO$  (detection limit  $\leq 7$  pptv) and  $NO_2$  (detection limit  $\leq 0.5$  ppbv) (Matveev et al., 2001).  $NO_y$  species ( $NO_y = NO_x + HNO_3 + 2N_2O_5 + NO_3 + \text{organic nitrates} + \text{particulate nitrate} + \dots$ ) were detected by the use of an appropriate converter located before the inlet  
15 of the  $NO_x$  monitor. This, together with  $NO_2$  data from the DOAS, was used to calculate the  $NO_z$  ( $NO_z = NO_y - NO_x$ ) concentrations. During another campaign at the Ein Bokek site canister samples were collected and analyzed for hydrocarbons using GCMS.

## 3 Results and discussion

### 3.1 The influence of $NO_2$ on the diurnal profiles of $BrO_x$ , $BrO$ and $Br$

20 The role of  $NO$  is not discussed in this section, because the  $NO$  levels measured during the field campaigns were usually very low, and frequently dropped to below detection limit (0.1 ppbv) during RBS activity. Additionally, the simulations showed that at these levels, the influence of  $NO$  on RBS activity was insignificant. In contrast,  $NO_2$  plays a significant role in the RBS chemistry at the Dead Sea due to its relative high  
25 concentrations and its important contribution to the recycling of  $BrO_x$ .

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The relationship between  $\text{NO}_2$  and BrO during daytime is shown in Fig. 1a. An anti correlation trend between the two can be observed, shown more distinctly in the insert (Fig. 1b). The anticorrelation between the two is in agreement with measurements (Fig. 9 in Tas et al., 2006). The insert represents the time period between 07:30 and 18:00 LT in order to exclude the  $\text{NO}_2$  peak occurring around 07:00 LT due to advection from the Dead Sea Works and the diminished BrO formation after 18:00 LT. The strong non-linear jagged shape of both  $\text{NO}_2$  and BrO is very obvious. Both the anticorrelation between BrO and  $\text{NO}_2$  and their jagged shape can be explained by the periodic two stage cyclic process previously described in detail in Tas et al. (2006), and summarized as follows: At the first stage an increase in ozone concentrations leads to an increase in the rate of BrO production via reaction (G2). This in turn leads to greater production of  $\text{BrO}_x$ , mainly through Cycle 3b, which then leads to the depletion of  $\text{O}_3$  during the second stage of this periodic process. As  $\text{O}_3$  levels drop below  $\sim 1$  to 2 ppbv, Br levels decrease further, due to increased tendency to form terminator species, in competition with its reaction with  $\text{O}_3$  (reaction G2) (see Fig. 2). As a result of the decrease in Br concentrations, ozone concentrations increase due to advection, initiating the periodic two stage cyclic process again.

The increase in Br and BrO levels during the first stage leads to a decrease in the concentrations of  $\text{NO}_2$ . This is mainly due to a higher rate of consumption of  $\text{NO}_2$  to form  $\text{HNO}_3$  via Cycle 3b, and to a lesser extent due to an enhancement in the formation of  $\text{BrONO}_2$  and  $\text{BrNO}_2$  (Tas et al., 2006). Thus, during this stage of the periodic process,  $\text{NO}_2$  tends to decrease while BrO tends to increase. During the second stage of the process a decrease in BrO and Br concentrations occurs and thus leads to a decrease in  $\text{NO}_2$  consumption rate, due to a slower rate of formation of  $\text{HNO}_3$ ,  $\text{BrONO}_2$  and  $\text{BrNO}_2$ . Thus, during this stage of the periodic process,  $\text{NO}_2$  increases while BrO tends to decrease. Thus, the two stages process leads to a jagged shape in the diurnal profiles of BrO and  $\text{NO}_2$  with an anti-correlation between the two.

The relationship between the termination reactions of RBS activity, represented by the terminator product HBr, and the mixing ratios of  $\text{O}_3$ ,  $\text{NO}_2$ , Br and BrO is shown

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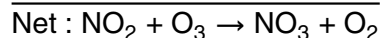


in Fig. 2. It can be seen that, with an analogy to the above explanations, when O<sub>3</sub> levels dip below ~2 ppbv, there is an increase in the mixing ratios of HBr (Fig. 2a and c), which is the main Br termination product. Figure 2c also shows that during intense RBS activity (between 08:00–18:30 LT), NO<sub>2</sub> correlates with HBr mixing ratios. The NO<sub>2</sub> peak around 07:00 LT, is a result of advection for that day, and is an exception. The correlation between NO<sub>2</sub> and HBr is the result of the tendency of these two species to increase as ozone mixing ratios drop below ~2 ppbv during the second stage of the periodic process, and to decrease during the first stage of the periodic process.

At noontime O<sub>3</sub> tends to reach nearly zero concentrations as some of the main bromine terminator species (i.e., HO<sub>2</sub> and CH<sub>2</sub>O) reach maximal concentrations. As a result, the depletion of BrO around noontime was repeatedly detected at the Dead Sea area (See Tas et al., 2006, Fig. 5). The relatively high rate of reaction of Br with its terminators during noon time causes the sharp increase in HBr between 10:30 a.m. and 12:30 p.m., simultaneous with Br and BrO depletion and NO<sub>2</sub> increase, as a part of the periodic process (Fig. 2b and c). This contradicts the predictions by von Glasow et al. (2002) that at the Dead Sea, in contrast to other sites, depletion of BrO will not occur during noontime due to the high BrO levels. Their assumption might still be correct for other areas of the Dead Sea, in which the depletion in O<sub>3</sub> is not as intense as it is at the evaporation ponds.

Cycle 4, in addition to Cycle 3, is another important chemical pathway for the recycling of BrO<sub>x</sub> via interaction with NO<sub>2</sub>:

### Cycle 4



Model simulations show that under the conditions prevalent at the Dead Sea the rates of cycles 4 and 3a are about the same. Cycles 4 and 3a are less important, in terms of  $O_3$  destruction, compared to Cycle 3b, which leads to an exponential net production of Br. However, these cycles (4 and 3a) are important due to their contribution to recycling of  $BrO_x$ , while preserving the bromine in the form of BrO, so that it can continue to react through Cycle 3b.

The direct reaction of  $NO_2$  with Br via reaction G9 leads to a null chemical pathway, since the produced  $BrNO_2$  is rapidly photolyzed to give the original reactants as shown in Cycle 5:

#### Cycle 5



In contrast to cycles 3a and 4, Cycle 5 preserves the bromine in the form of Br, and thus tends to decrease the formation rate of  $BrO_x$  via Cycle 3b. During the second stage of the periodic process, the rate of reaction G9 increases in parallel with a simultaneous decrease in the rate of ozone destruction (reaction G2) (Fig. 3a and inset 3a'), reflecting the increase of cycle 5 at the expense of cycles 3 and 4. The rate of reaction G9 increases because less ozone is available to react with Br, and also because of the increase in the ratio  $[Br]/[BrO]$ . Because, at this stage,  $NO_2$  has a greater tendency to react with Br than with BrO, the rate of reaction G7 also decreases, in parallel with the increase in reaction G9 and the decrease in reaction G2 (Fig. 3b). Figure 3 shows that the depletion in the rates of reactions G2 and G7 and the increase in reaction G9, are most significant when  $O_3$  mixing ratios drop below the threshold level of about 1 to 2 ppbv.

The influence of  $O_3$  levels on the relative rates of reactions G7 and G9 has an important influence on the way that  $NO_2$  interacts with  $BrO_x$ . A decrease in  $O_3$  leads to an

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increase in the ratio  $[\text{Br}]/[\text{BrO}]$ , a consequent increase in the rate of reaction G9 relative to the rate of reaction G7, and therefore to a lower rate of reactions through cycles 3 and 4 relative to the rate of reactions through Cycle 5. This leads to a decrease in the growth of BrOx mixing ratios and therefore a decrease in the destruction rate of  $\text{O}_3$ , and a lower rate of increase in the mixing ratios of  $\text{NO}_2$  (Fig. 2). In contrast, an increase in  $\text{O}_3$  levels leads to a higher rate of  $\text{NO}_2$  reaction via cycles 3 and 4 relative to the rate of reactions through Cycle 5. This results in an increase in the mixing ratios of BrOx, and therefore an increase in the destruction rate of  $\text{O}_3$  and a simultaneous decrease in the mixing ratios of  $\text{NO}_2$  (Fig. 2).

### 3.2 The influence of $\text{NO}_2$ on the daily average levels of $\text{BrO}_x$

As discussed in the previous section, the tendency of  $\text{NO}_2$  to react, during daytime, through Cycle 3b, as well as cycles 3a and 4, rather than Cycle 5, greatly enhance the formation of BrOx and ozone destruction. In this section the investigation is limited only to the influence of  $\text{NO}_2$  concentrations on the daily (06:00–20:00 LT) average concentrations of BrO, Br,  $\text{BrO}_x$  and  $\text{O}_3$  during RBS activity. Its influence on the diurnal profile of these species is ignored.

The influence of different levels of  $\text{NO}_2$  on BrOx concentrations was examined for 11 simulations with various levels of  $\text{NO}_2$  fluxes. These simulations were based on the parameters of the “FULL” simulation (Sect. 2) as a base case scenario, and changing only the  $\text{NO}_2$  flux levels. For each of these simulations, the value of the  $\text{NO}_2$  flux was multiplied by a single factor at each update time (every 15 min). Each of the 11 scenarios was run using a different multiplication factor,  $n$ , which was varied from 0.1 to 100, where  $n$  is the value by which the  $\text{NO}_2$  fluxes of the “FULL” simulation were multiplied. Each of the 11 simulations was run again under the same conditions, except that the bromine mechanism was excluded. Thus, for example, a simulation that was run with  $n=1$ , represents the “FULL” simulation if the bromine mechanism was included and the “NOB” simulation (Sect. 2) if the bromine mechanism was not included.  $n=40$  denotes  $\text{NO}_2$  fluxes 40 times larger than those given by the “FULL” or “NOB” base case

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simulations. Table 1 shows the daily average mixing ratios of some species and NO<sub>2</sub> fluxes during RBS activity (06:00–20:00 LT) obtained for the different simulations.

Figure 4 shows the results for the eleven simulations relating to the variations in BrO<sub>x</sub>, Br and BrO levels with increasing NO<sub>2</sub> levels obtained for the 11 simulations that are based on the “FULL” simulations. Roughly, for Br and BrO<sub>x</sub>, the results of these simulations show two distinct zones of influence with respect to the NO<sub>2</sub> levels, separated at approximately  $n=40$ . In the lower zone, the Br and BrO<sub>x</sub> concentrations increase sharply until  $n=10$  and less strongly until  $n=40$ , reaching peak values of 0.2 and 0.25 ppb, respectively. From this point onwards there is a slow decrease in concentrations for both Br and BrO<sub>x</sub>. In contrast, the BrO shows a continuous decrease in levels from a value of around 0.04 ppb at  $n=0.1$ , to half that value at  $n=100$ . Thus, the increase in BrO<sub>x</sub> at the lower zone is due to the strong increase in Br that more than compensates for the decrease in BrO (see Table 1 and Fig. 4).

In the lower zone, the increase in NO<sub>2</sub> leads to an increase in the rate of reactions through Cycle 3b and hence to an increase in the concentrations of Br and BrO<sub>x</sub>. The reason for the decrease in the production rate of Br and BrO<sub>x</sub> in the lower zone, for  $n>10$ , and for the decrease in their concentrations at the higher zone, is related to the increase in the tendency of NO<sub>2</sub> to react through Cycle 5 relative to its tendency to react through cycles 3 and 4 for higher NO<sub>2</sub> fluxes. As was explained in Sect. 3.1, the tendency of NO<sub>2</sub> to react through cycles 3 and 4, relative to the rate of reactions through Cycle 5, is determined mainly by the [Br]/[BrO] ratio, which is highly sensitive to variations in O<sub>3</sub> levels. For  $n<10$  the ozone concentrations are still high and thus the ratio [Br]/[BrO] (Fig. 5b) is relatively low, and the rate of reactions through Cycles 3 and 4 is high relative to the rate of reactions through cycle 5. Thus, in this range a sharp increase in the concentrations of Br and BrO<sub>x</sub> occurs as a result of the increase in NO<sub>2</sub> fluxes (Fig. 4 and Table 1). However, Fig. 6 (see below) shows that this ratio constantly increases for higher  $n$  values, and hence an increase in the formation of BrNO<sub>2</sub> occurs at the expense of BrO<sub>x</sub> production via Cycle 3b.

The question raised at this stage is the reason for the increase in the ratio [Br]/[BrO]

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and the consequent decrease in Br and BrO<sub>x</sub> concentrations, for increasing n values at the higher range. Figure 5 shows that an increase in the ratio [Br]/[BrO] cannot be solely the result of the increase in ozone levels, since above  $n=20$  this ratio increases in parallel with the ozone concentrations (Fig. 5a). The increase in the ratio [Br]/[BrO] is the result of the production of Br at the expense of BrO, due to the higher rate of reactions through Cycle3b as the NO<sub>2</sub> levels are higher. The increase in the ratio [Br]/[BrO] leads to an increase in the rate of reactions through Cycle 5 relative to the rate of Cycles 3 and 4, and thus to an enhancement of the production of BrNO<sub>2</sub> at the expense of BrONO<sub>2</sub>. Thus, the increase in the concentrations of NO<sub>2</sub> cannot lead to an unlimited increase in the concentrations of Br and BrO<sub>x</sub>, since the increase in the formation of Br leads to production of BrNO<sub>2</sub> at the expense of BrO<sub>x</sub> production, above a certain level of NO<sub>2</sub>.

Figure 5 further demonstrates the complex influence of NO<sub>2</sub> on BrO<sub>x</sub> levels. Figure 5c shows the variation in mixing ratios of BrONO<sub>2</sub> and BrNO<sub>2</sub> with increasing NO<sub>2</sub> flux. The increase in the ratio [BrNO<sub>2</sub>]/[BrONO<sub>2</sub>] for higher n values (Fig. 5b), is the result of the increase in the ratio [Br]/[BrO], and reflects an increase in the formation of the reservoir BrNO<sub>2</sub> through Cycle 5, at the expense of the enhancement of BrO<sub>x</sub> production and BrO recycling through cycles 3 and 4, respectively. At a certain stage the rate of reactions through Cycle 5 become predominant relative to the rate of reactions through Cycle 3b. This leads to a decrease in the growth of Br and BrO<sub>x</sub> concentrations above  $n=10$  and to a decrease in their concentrations above  $n=40$ .

The constant increase in BrONO<sub>2</sub> reflects the constant increase in the rate of reactions through Cycle 3b for higher n values, which leads to the increase in the concentrations of the total bromine (Br<sub>t</sub>) species (Fig. 5d). However, although Br<sub>t</sub> increases at higher n values, the increase in the formation of BrNO<sub>2</sub> via Cycle 5 dominates the BrO<sub>x</sub> production above  $n\sim4$ , and leads to a decrease in the ratio [BrO<sub>x</sub>]/[Br<sub>t</sub>].

The influence of the increase in NO<sub>2</sub> concentrations on ozone destruction via BrO<sub>x</sub> production is demonstrated in Fig. 6. This figure shows the average ozone mixing ratios with and without the effect of bromine chemistry. Under the full bromine chemistry

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conditions the average ozone levels show a continuous drop for increases in  $n$  values, reaching minimum levels ( $\sim 1$  ppb) at  $n=20$ . It should be remarked that the reduction in  $O_3$  levels in this lower  $NO_2$  zone occurs under  $NO_x$  limited conditions in terms of the efficiency of photochemical ozone production. Above  $n=20$ , ozone levels continuously increase due to the decrease in  $BrO_x$  levels. Between  $n=20$  and 40 there is an increase in  $O_3$  levels although the  $BrO_x$  levels increase. This increase is due to the greater contribution of  $NO_2$  to form  $O_3$  via photochemical processes, in comparison with its contribution to  $O_3$  destruction as a result of  $BrO_x$  formation. In contrast, when no bromine chemistry is active, the ozone concentrations increase with increasing  $NO_2$ , since the system is  $NO_x$  limited. However from levels above  $n=40$  a sharp decrease in ozone levels is observed, due to titration between  $O_3$  and  $NO$ . From this point forward the ozone concentrations remain almost constant.

The analysis presented in this section shows that an increase in the growth of  $BrO_x$ , as a result of an increase in  $NO_2$  levels, occurs for a wide range of  $NO_2$  concentrations, representing a wide range of anthropogenic pollution levels (see Table 1). Thus, also in other areas in which the heterogeneous decomposition of  $BrONO_2$  and the “Bromine Explosion” mechanism occur efficiently enough, an increase in  $NO_2$  concentrations should result in an increase in  $BrO_x$  concentrations and a consequent depletion in ozone concentrations.

In other cases for which these two processes do not occur efficiently enough, the increase in the concentrations of  $NO_x$  can lead to continues decrease in the concentrations of  $BrO_x$ . For example, several studies (e.g., Beine et al., 1997; Sander et al., 1999; Ridley and Orlando., 2003) have showed that an increase in the concentrations of  $NO_x$  impedes the destruction of ozone due to its tendency to form reservoirs by interaction with  $BrO_x$ . Thus, simultaneous depletions in ozone and  $NO_x$ , during ODE’s were explained by the higher impact of RBS activity on reduction in ozone levels due to a decreased tendency to form bromine containing nitrogen reservoirs, as the  $NO_x$  levels are lower. It should be remarked that these simultaneous depletions in  $NO_x$  (representing mainly depletion in  $NO_2$ ) and ozone concentrations might also be the result

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of the heterogeneous decomposition of  $\text{BrONO}_2$  that may lead to both  $\text{NO}_2$  depletion (e.g., Tas et al., 2006; Morin et al., 2007) and ozone destruction via  $\text{BrO}_x$  formation. The significant influence of heterogeneous recycling of  $\text{BrONO}_2$  on the way that an increase in the  $\text{NO}_x$  concentrations influences RBS activity was also demonstrated by von Glasow et al. (2003). Their study showed that when the total surface area of particles available for the recycling of  $\text{BrONO}_2$  and  $\text{HBr}$  is high enough, the transformation of RBS into bromine-containing nitrogen reservoirs is significantly reduced.

It has been shown in this section that even in cases where the two heterogeneous processes, the “Bromine Explosion” mechanism and the heterogeneous decomposition of  $\text{BrONO}_2$  take place in the chemical mechanism, increasing  $\text{NO}_2$  cannot continue to increase the concentrations of  $\text{BrO}_x$  indefinitely. Above a certain threshold value of  $\text{NO}_2$ , the concentrations of  $\text{BrO}_x$  are predicted to decrease. According to the present research, under conditions typical of the Dead Sea, this threshold value averages 0.2 ppbv during 06:00–20:00 LT time period (see Table 1). This value is equivalent to an average  $\text{NO}_2$  concentration of about 2.1 ppbv, for the same conditions without the bromine mechanism. This threshold value is influenced by many factors. Basically, a decrease in  $\text{BrO}_x$ , for an increase in  $\text{NO}_2$  levels, is predicted to occur only if  $\text{O}_3$  levels are low enough in order to enable a low enough  $[\text{Br}]/[\text{BrO}]$  ratio. The  $[\text{Br}]/[\text{BrO}]$  ratio and hence also the threshold value are sensitive to other parameters, including the total surface area available for heterogeneous decomposition of  $\text{BrONO}_2$ , the rate of bromine release into the gas phase, etc. Thus, the threshold level of  $\text{NO}_2$  should be different at other locations.

An earlier study (Sander et al., 1999) suggested that an increase in  $\text{NO}_2$  levels did not result in a higher contribution to  $\text{BrO}_x$  production by the heterogeneous decomposition of  $\text{BrONO}_2$ . The reason given for that (Sander et al., 1999) was that the higher levels of  $\text{NO}_2$  led to a significant increase in the reaction rates of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  with  $\text{Br}^-$  via the heterogeneous reactions (H3) and (H4):



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In contrast, under the conditions at the Dead Sea, which were also used by the “FULL” simulation, the daytime levels of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  remained in the sub-ppt level. For example, for the “FULL” conditions the  $\text{NO}_3$  levels were at least two orders of magnitude smaller than  $\text{NO}_2$ , while  $\text{N}_2\text{O}_5$  levels were four orders of magnitude smaller than  $\text{NO}_2$  levels. Thus, it appears that under the conditions represented by the present study, reactions (H3) and (H4), which involve  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ , can be neglected in comparison with reaction H1.

## 4 Summary

The influence of  $\text{NO}_2$  on both the diurnal profiles and daily average production of Br and BrO was investigated in this study, based on measurements performed at the evaporation ponds at the Dead Sea. It has been shown that the ratio  $[\text{Br}]/[\text{BrO}]$  has a significant influence on the way that  $\text{NO}_2$  influences both the diurnal profiles and average daily production of Br and BrO. Higher levels of  $[\text{Br}]/[\text{BrO}]$  lead to a decrease in the concentrations of  $\text{BrO}_x$  during the day and on a daily average basis. This is because higher levels of  $[\text{Br}]/[\text{BrO}]$  lead to higher rates of reactions of  $\text{NO}_2$  through Cycle 5 relative to the rate of reactions through cycles 3 and 4. During the daytime, higher levels of ozone were the major factor causing an increase in the production of  $\text{BrO}_x$  by decreasing the ratio  $[\text{Br}]/[\text{BrO}]$ . However, for higher  $\text{NO}_2$  levels and on a daily average basis, the  $\text{NO}_2$  concentrations were the major factor to influence the  $\text{BrO}_x$  concentrations by changing the  $[\text{Br}]/[\text{BrO}]$  ratio, while ozone had only a secondary effect on this ratio.

The present study shows that the influence of  $\text{NO}_2$  on the daily average  $\text{BrO}_x$  production, can be divided into two main zones of  $\text{NO}_2$  levels, separated by a certain threshold value of  $\text{NO}_2$  concentrations. According to the present research, under the Dead Sea conditions this threshold value equals about 0.2 ppbv on a daily (06:00–

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20:00 LT) average. This value is equivalent to a daily average concentration of  $\text{NO}_2$  of about 2.1 ppbv, for the same conditions excluding the bromine mechanism. In other geographical locations the value of this threshold level is expected to be different because it depends on many parameters, including the total surface area available for heterogeneous decomposition of  $\text{BrONO}_2$ , among other factors.

In the lower zone, below the threshold level of  $\text{NO}_2$ , an increase in  $\text{NO}_2$  leads to a higher production of  $\text{BrO}_x$ , which results in more intensive destruction of  $\text{O}_3$ , as a result of an increase in the rate of reactions through cycles 3 and 4 relative to the rate of reactions through Cycle 5. For higher  $\text{NO}_2$  levels the rate of Cycle 5 relative to cycles 3 and 4 becomes higher until, above a certain threshold level of  $\text{NO}_2$ , an additional increase in  $\text{NO}_2$  levels leads to a decrease in  $\text{BrO}_x$  levels and  $\text{O}_3$  destruction. It is demonstrated by the present study that, on a daily average basis, above a certain threshold level of  $\text{NO}_2$ , an increase in the concentrations of  $\text{NO}_2$  leads to a decrease in the  $\text{BrO}_x$  concentrations, in a self-terminating process.

One of the most significant contributions of the present study refers to the relation between anthropogenic activity and RBS activity. It was shown that an increase in the concentrations of  $\text{NO}_2$  leads to an enhancement of ozone destruction via an increase in the concentrations of  $\text{BrO}_x$  for a relatively wide range of  $\text{NO}_2$  levels, reflecting different levels of anthropogenic activity. Similar influence of anthropogenic activity on RBS activity is expected to occur in other areas that are under the influence of anthropogenic activity, in which the heterogeneous decomposition of  $\text{BrONO}_2$  and the release of bromine into the gas phase activated by  $\text{HOBr}$  are involved in the chemical mechanism. It should be remarked that in other areas in which these two processes, are not significant enough, the increase in  $\text{NO}_x$  levels may cause a decrease in ozone destruction rates due to the formation of bromine-containing nitrogen reservoirs.

The present study shows that, on a daily average basis and for all levels of  $\text{NO}_2$  that were investigated, the levels of the total bromine species in the gas phase increase for higher  $\text{NO}_2$  levels, as the result of an absolute increase in the rate of Cycle 3b. In the higher zone, the formation of  $\text{BrNO}_2$  is favored at the expense of  $\text{BrO}_x$ . Once the

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ozone concentrations increase again, this reservoir may undergo fast photolysis during daytime, thereby increasing the concentrations of  $\text{BrO}_x$ .

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**Table 1.** Average (06:00–20:00 LT time period) concentrations of various species obtained for NO<sub>2</sub> different levels.

Multiplication factor ( <i>n</i> ) for NO <sub>2</sub> fluxes*	BrO (ppbv)	Br (ppbv)	NO <sub>2</sub> (ppbv)	O <sub>3</sub> (ppbv)	NO <sub>2</sub> ** (NOB) (ppbv)	O <sub>3</sub> ** (NOB) (ppbv)
0.1	0.0444	0.0523	0.0424	4.81	0.795	70.3
0.125	0.0444	0.0526	0.0425	4.80	0.797	70.4
0.167	0.0444	0.0531	0.0426	4.77	0.798	70.5
0.25	0.0444	0.0541	0.0430	4.71	0.801	70/6
0.5	0.0445	0.0575	0.0436	4.44	0.809	71.0
1	0.0445	0.0651	0.0439	4.20	0.825	72.0
2	0.0445	0.0824	0.0450	3.60	0.857	73.7
4	0.0438	0.121	0.0518	2.80	0.922	76.9
6	0.0412	0.153	0.0631	2.02	0.984	79.8
8	0.0406	0.184	0.0767	1.33	1.05	82.5
10	0.0395	0.193	0.0964	1.08	1.11	85.0
20	0.0381	0.199	0.211	1.02	1.47	95.4
40	0.0328	0.223	0.194	1.52	2.05	109
60	0.0294	0.211	0.921	2.25	76.9	229
80	0.0250	0.196	1.39	2.98	98.3	213
100	0.0238	0.182	1.89	3.69	115	198

\* The “*n*” factors represent the values by which the NO<sub>2</sub> fluxes included in the “FULL” simulation were multiplied (see Sect. 3.2). The average NO<sub>2</sub> flux used for “FULL” simulation is  $3.61 \cdot 10^{13}$  molec/m<sup>2</sup> during RBS activity (06:00–20:00 LT).

\*\* Mixing ratios obtained during “NOB” simulation.

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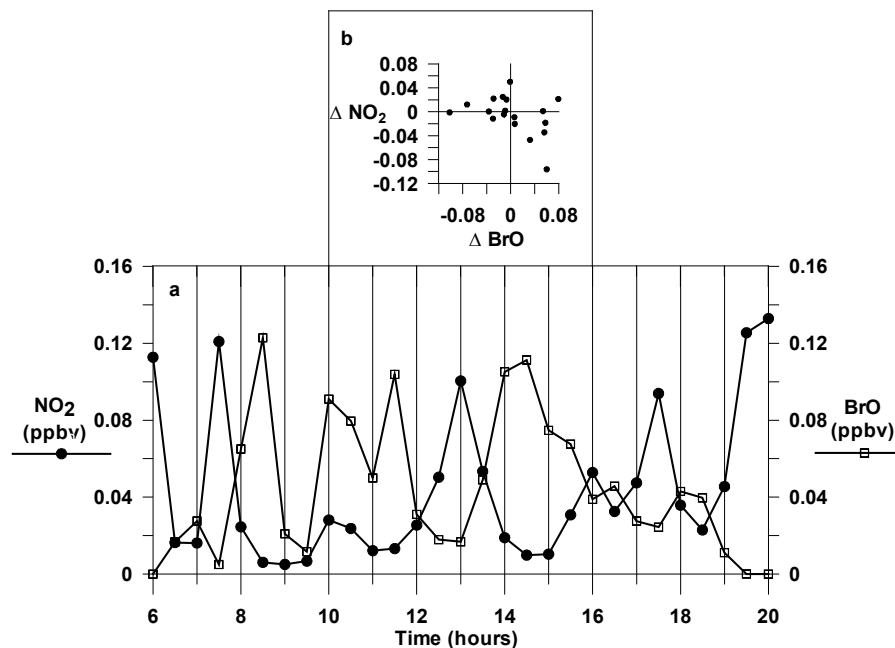
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**Fig. 1.** Simulated mixing ratios of  $\text{BrO}$  and  $\text{NO}_2$ . **(a)**  $\text{BrO}$  and  $\text{NO}_2$  diurnal profiles obtained for “FULL” simulation. **(b)** The difference in  $\text{NO}_2$  mixing ratios between each two following time points was calculated and presented vs. the concurrent difference in  $\text{BrO}$  mixing ratios. The graph shows the data between 07:30–18:00 LT.

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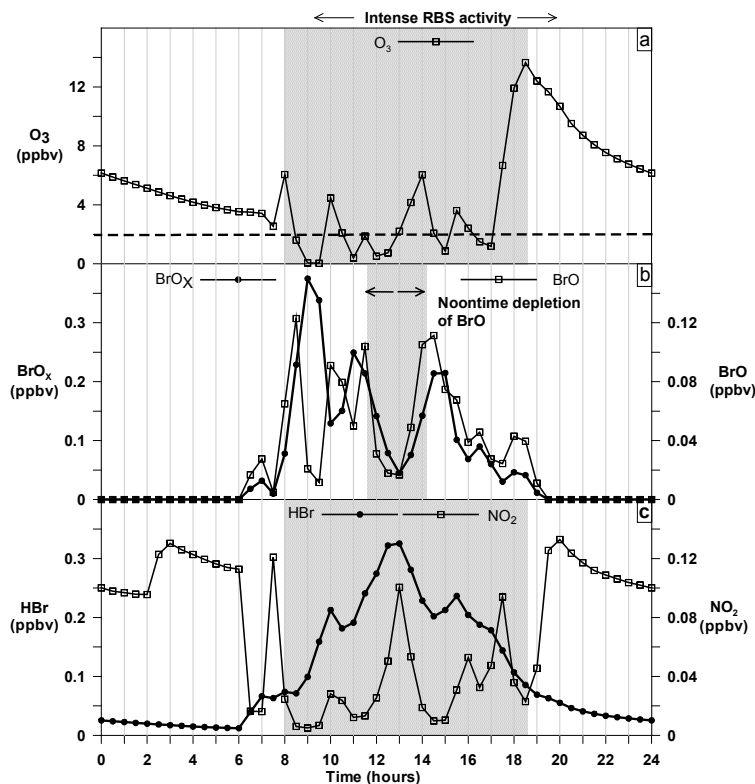
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**Fig. 2.** The influence of O<sub>3</sub> depletion below ~1–2 ppbv on BrO, BrO<sub>x</sub> and NO<sub>2</sub> diurnal profiles\*. **(a)** When O<sub>3</sub> levels are reduced below ~1–2 ppbv, mixing ratios of HBr increase, indicating an increase in the rate that Br undergoes termination reactions (c). **(b)** This in turn causes the decrease in Br and BrO mixing ratios, and hence leads to lower BrO<sub>x</sub> levels. **(c)** The decrease in Br and BrO mixing ratios as O<sub>3</sub> dip below ~1–2 ppbv leads to an increase in NO<sub>2</sub> mixing ratios, due to lower consumption rate by Br and BrO. This is the reason for the positive correlation between NO<sub>2</sub> and HBr. The increase in the mixing ratios of NO<sub>2</sub> and HBr is most significant during the noontime, as the mixing ratios of Br and BrO are depleted.

\* All presented diurnal profiles were obtained during “FULL” simulation. The shaded area in **(a)** and **(c)** refers to intensive RBS activity, while the shaded area in **(b)** refers to noontime (see Sect. 3.1).

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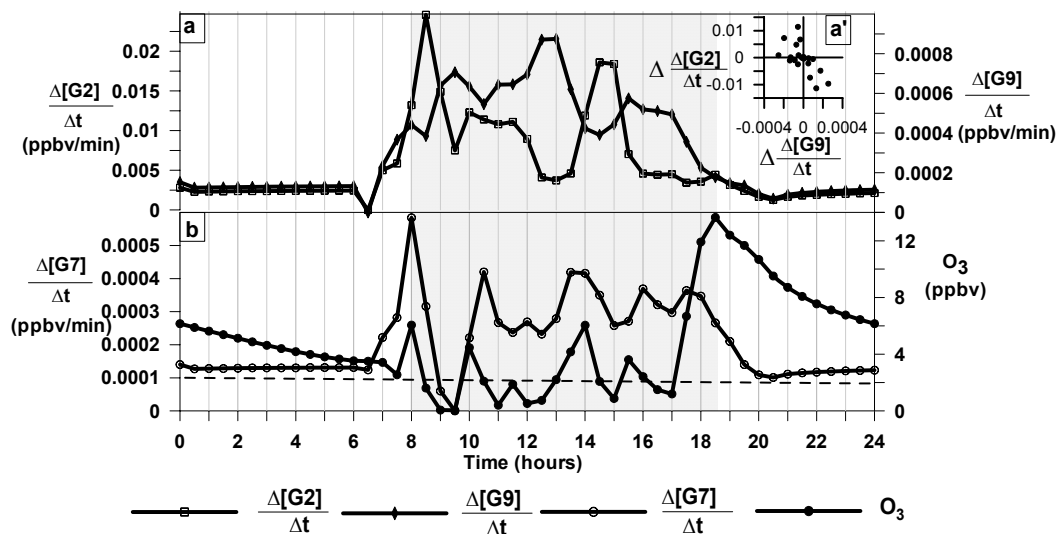
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**Fig. 3.** The influence of ozone levels on the relative tendencies of NO<sub>2</sub> to react through cycles 3, 4 and 5\*. **(a)** During the second stage of the periodic process as intensive RBS take place (indicated by the shaded areas in plots a and b) a decrease in the rate of reaction G2 and an increase in the rate of reaction G9 occur, as a result of the decrease in ozone mixing ratios, below the level of ~1 to 2 ppbv, and a consequent increase in the ratio [Br]/[BrO]. The insert 3.a' presents the difference in reaction rate G2 between each two following time points versus the compatible differences in the values of the rate of reaction G9. This graph relates only to values that were obtained during RBS activity (06:00–20:00 LT). **(b)** The phenomena described above occur most significantly as a decrease in ozone mixing ratios below the threshold level of ~1 to 2 ppbv occurs. Due to the increase in the ratio [Br]/[BrO] during the second stage, the rate of reaction G7 also decreases parallel to the decrease in the rate of reaction G2 and the increase in the rate of reaction G9.

\* All presented diurnal profiles were obtained during “FULL” simulation.

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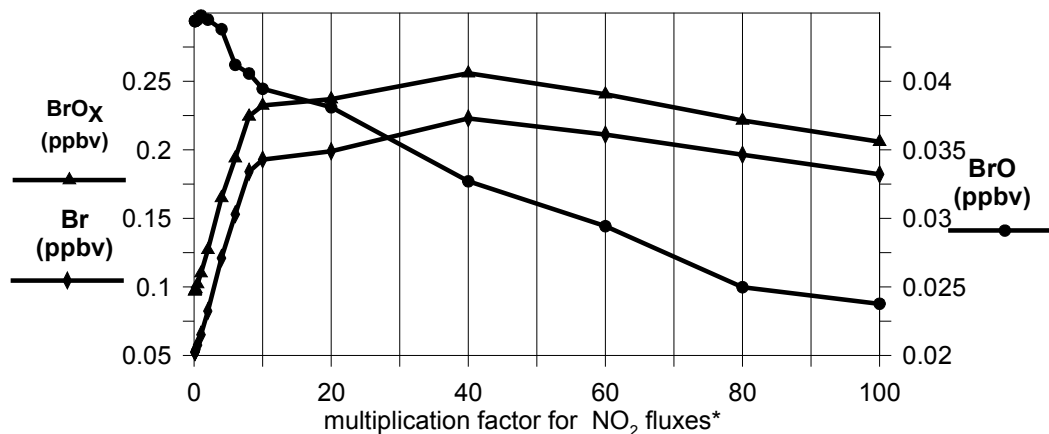
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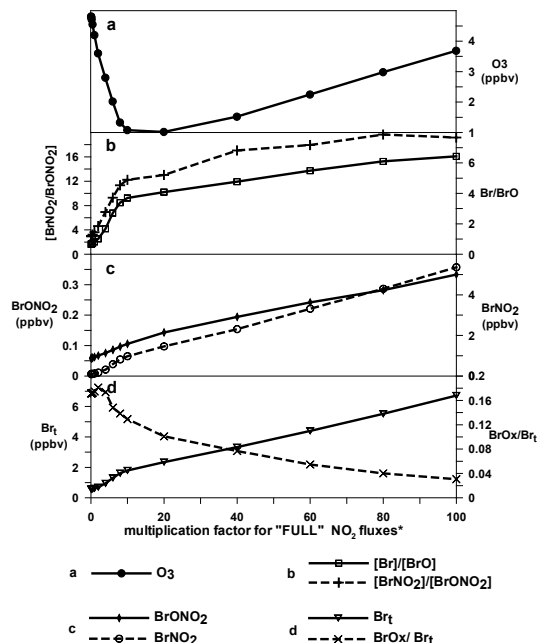
**Fig. 4.** Br, BrO and BrO<sub>x</sub> mixing ratios as a function of NO<sub>2</sub> flux magnitude. The mixing ratios of Br, BrO and BrO<sub>x</sub> obtained for the 11 simulations based on the “FULL” simulation are presented versus the multiplication factor for NO<sub>2</sub> fluxes,  $n^*$ . Two zones can be observed for changes in Br and BrO<sub>x</sub> concentrations, separated in the graph at  $n=40$ . In the lower zone Br and BrO<sub>x</sub> increase sharply until  $n=10$ . In contrast, BrO concentrations decrease sharply from  $n<1$ .

\* See additional information on the multiplication factor,  $n$ , in Sect. 3.2.

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**Fig. 5.** Production of BrO<sub>x</sub> and total bromine species as a function of NO<sub>2</sub> fluxes. **(a)** O<sub>3</sub> mixing ratios obtained for the 11 simulations that included the “FULL” bromine mechanism. O<sub>3</sub> concentrations decrease for an increase in  $n$  values until around  $n=20$ . The increase in the concentrations of O<sub>3</sub> for  $n \gtrsim 20$  indicates that the ratio  $[\text{Br}]/[\text{BrO}]$  is not influenced only by the O<sub>3</sub> concentrations. **(b)** The ratio  $[\text{Br}]/[\text{BrO}]$  constantly increase for an increase in  $n$  levels, mainly as a result of the higher rate of reactions through cycle 3b that lead to production of Br at the expense of BrO. The increase in the ratio  $[\text{Br}]/[\text{BrO}]$  leads to an increase in the ratio  $[\text{BrNO}_2]/[\text{BrONO}_2]$ , for higher  $n$  values. This reflects an increase in the rate of reactions through Cycle 5 relative to the rate of reactions through cycles 3 and 4. This, in turn, leads to a faster production of BrNO<sub>2</sub> via Cycle 5 at the expense of BrO<sub>x</sub> production and recycling via cycles 3b and 3a and 4, respectively. At a certain stage the ratio  $[\text{Br}]/[\text{BrO}]$  is high enough, to cause a decrease in the concentrations of Br and BrO<sub>x</sub> for an increase in  $n$  values. **(c)** Both the concentrations of BrNO<sub>2</sub> and BrONO<sub>2</sub> constantly increase for an increase in  $n$  values. **(d)** The continuous increase in the concentrations of BrONO<sub>2</sub> leads to a continuous increase in Br<sub>I</sub>, for an increase in  $n$  values, due to an increase in the rate of Cycle 3b. The increase in the ratio  $[\text{BrNO}_2]/[\text{BrONO}_2]$  leads to an increase in the ratio  $[\text{Br}]/[\text{BrO}_x]$  above  $n \gtrsim 4$ , due to an increase in the rate of Cycle 5 relative to the rates of cycles 3 and 4.

\* See additional information on the multiplication factor,  $n$ , in Sect. 3.2.

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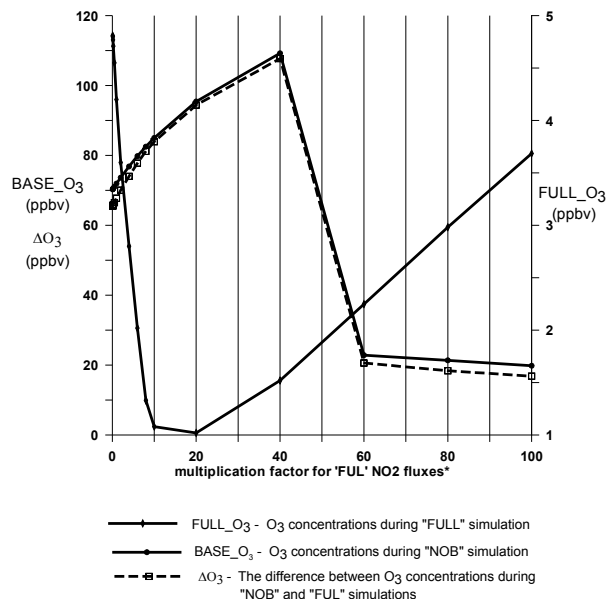
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**Fig. 6.** Destruction of ozone by RBS activity as a function of NO<sub>2</sub> flux magnitude. Presented are the O<sub>3</sub> mixing ratios obtained for the 11 simulations that includes the “FULL” bromine mechanism (FULL\_O<sub>3</sub>), the O<sub>3</sub> mixing ratios that were obtained during the 11 simulations that didn't include the bromine mechanism (BASE\_O<sub>3</sub>), and the difference between these two categories (ΔO<sub>3</sub>). The “FULL\_O<sub>3</sub>” concentrations decrease for  $n$  values smaller than 20 due to an increase in BrO<sub>x</sub> concentrations as a result of the increase in the rate of Cycle 3b. For these  $n$  values the “FULL\_O<sub>3</sub>” decrease although the “BASE\_O<sub>3</sub>” production is NO<sub>x</sub> limited in terms of photochemical ozone production. Between  $n=20$  and  $n=40$  an increase in “FULL\_O<sub>3</sub>” concentrations occurs although BrO<sub>x</sub> concentrations increase too. This should be the result of the more intense effect of NO<sub>2</sub> to increase O<sub>3</sub> due to the limited NO<sub>x</sub> conditions in terms of photochemical ozone production, compared to its effect to reduce O<sub>3</sub> as a result of increase in BrO<sub>x</sub> production.

\* See additional information on the multiplication factor,  $n$ , in Sect. 3.2.

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